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ON THE ABSORPTION SPECTRA OF Ni^{++} ION IN AQUEOUS SOLUTION

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(*Received July* 23, 1965 ; *Resubmitted June* 15, 1966)

ABSTRACT.. Oscillator strength of a dozen of nickel salts in aqueous solution were calculated following Van Vleck, Tanabe and Sugano, and Jörgensen from the absorption density measurements. It was observed that stronger the cubic portions of the crystal field the greater were the oscillator strength. The effect of the crystal field on oscillator strength provides a basis to say that the red band splitting is not due to first order L-S coupling or due to second order intermixing in agreement with the findings of Mookherji and Chhonkar that the splitting is due to tetragonal field.

INTRODUCTION

Considerable amount of experimental (Mookherji and Chhonkar 1959, 1960, Chhonkar 1964) and theoretical (Holmes and McClure 1957, Liehr and Ballhausen 1959, Englman 1961) work on the absorption spectra of Ni^{++} ions in state of solution and in crystalline state has been carried out. The characteristics of absorption bands are position, band width and intensity. The positions of absorpiton bands of Ni^{++} ions in aqueous solution and in different organic solvents have been cor- related to some details by the assumption of a crystalline electric field predominantly cubic in nature on which is superimposed a small tetragonal component. It was Mookherji and Chhonkar (1960) who first showed that the splitting of the red band into bands II and III was due to tetragonal field. Later on Bose and Chatterji (1963) applied a rhombic component instead of tetragonal in case of Ni^{++} ions in crystals and got a good agreement with the observed values of Hart-mann *et al* (1958.)

The intensity which is proportional to the area of the absorption curve and consequently proportional to the oscillator strength contains information as to the nature of the transition. The line shape gives us information about the environments of the absorbing ion. Our work (1964) on Ni^{++} ions in organic solvents definitely establishes that the cluster about Ni^{++} is more anisotropic than that in aqueous solution and hence the influence of environments. All the previous works were concerned with correlating the oscillator strength of these absorption bands as spin-forbidden spectral transitions taking the field as cubic in symmetry. Experimental findings of Krishnan and Mookherji (1938) do not support a cubic field. In order to understand the behaviour of variation of cubic

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field on the oscillator strength we have calculated the oscillator strength from the observed absorption density in a number of Nickel salts in aqueous solution in which the strength of cubic field coefficients varied considerably.

The present communication gives an account of the above studies.

EXPERIMENTAL

The experimental details have been discussed by Mookherji and Chhonkar (1959, 1960). For the study in the ultra-violet region the glass prism was replaced by a quartz prism. The measurements were carried out by using stoppered fused silica cells. The variations of absorption in different salt solution are shown graphically in fig 1 to 20. (Mookherji and Chhonkar 1960).

RESULTS

The results of measurements are collected in Table I. The oscillator strength P is given approximately by the relation (Jörgensen 1962)

$$P = 4.60\times10^{-9}\, E_n[\delta(-)+\delta(+)],$$

where E_n is the molar extinction coefficient. n is the band number and $\delta(-)$, $\delta(+)$ are half widths towards smaller and larger wave-lengths. E_n is given by $E_nCX = -\log(I/I_0)$ = absorption density. C is the concentration per mol per

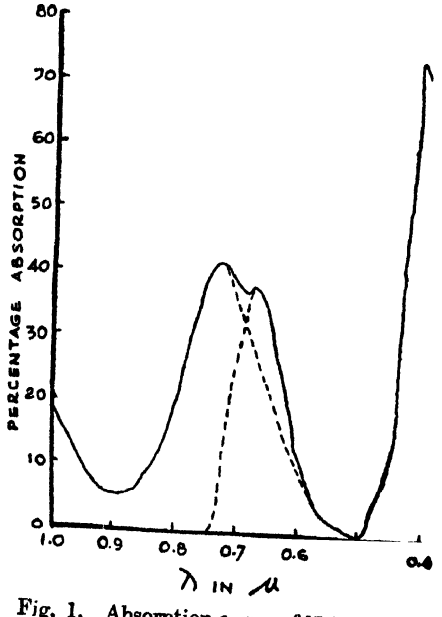

Fig. 1. Absorption curve of $NiSO_4$ solution (0.1068M).

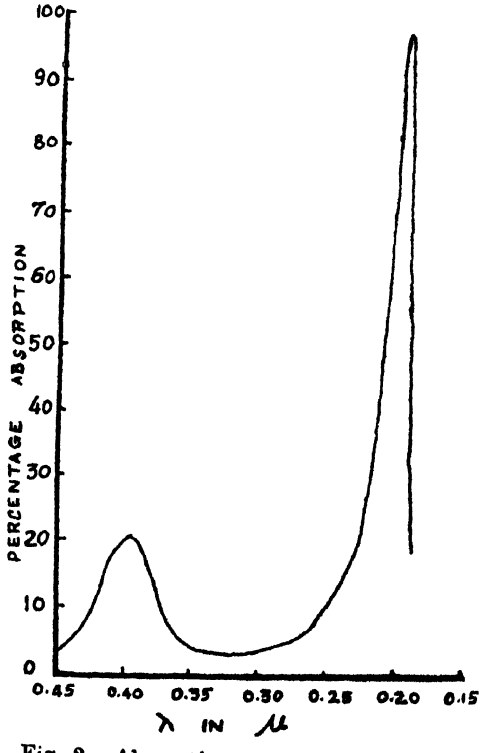

Fig. 2. Absorption curve of $NiSO_4$ solution (0.0178M).

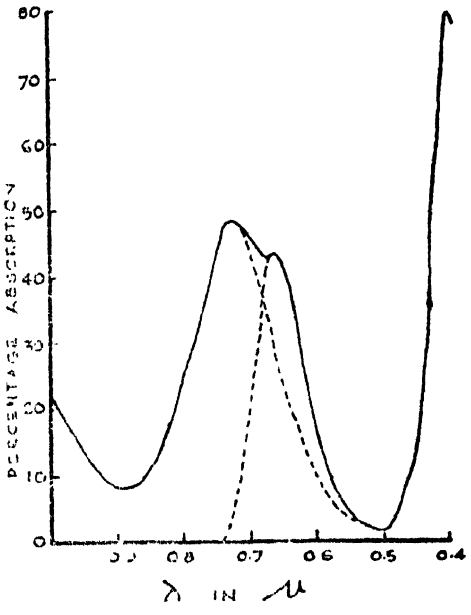

Fig. 3. Absorption curve of $NiSeO_4$ solution (0.129M).

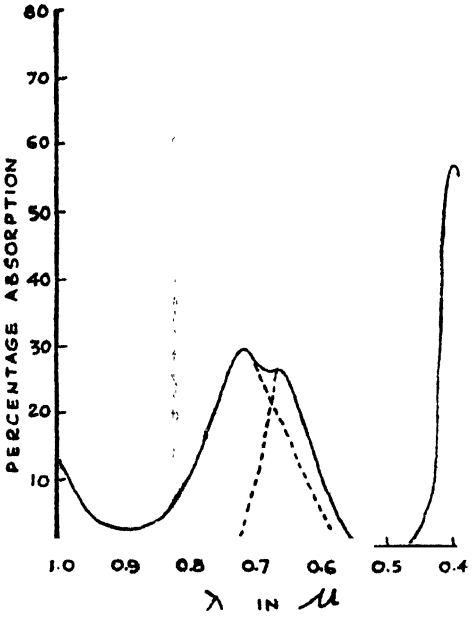

Fig. 4. Absorption curve of $Ni(NH_4SO_4)_2$ solution (0.076M).

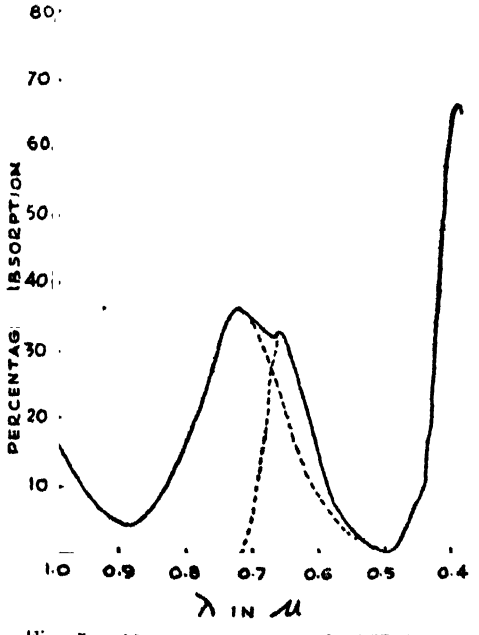

Fig. 5. Absorption curve of $Ni(K.SO_4)_2$ solution (0.0913M).

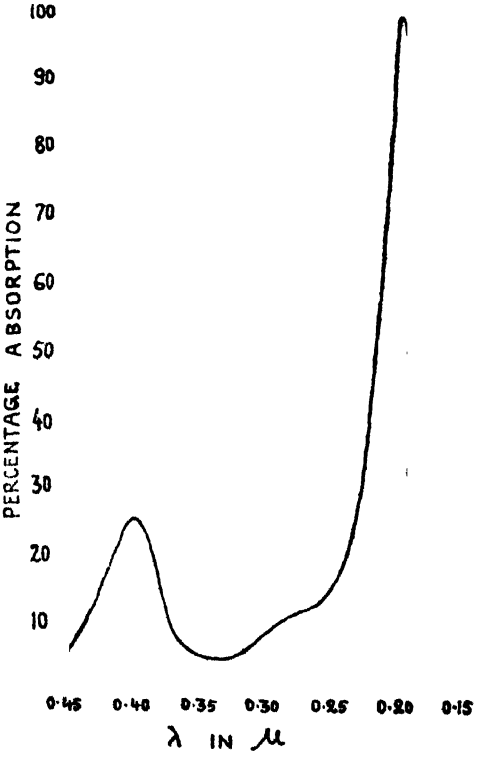

Fig. 6. Absorption curve of $Ni(K.SO_4)_2$ solution (0.0229M).

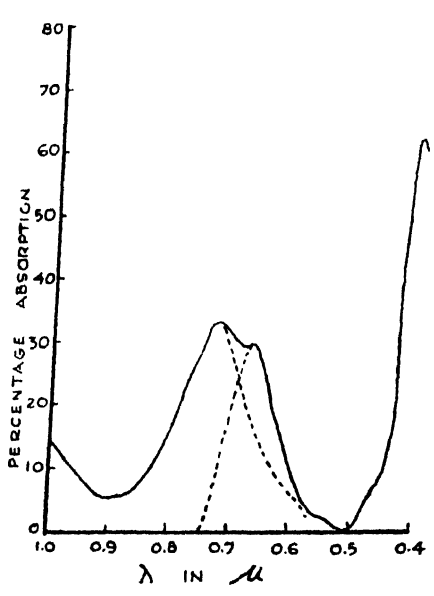

Fig. Absorption curve of $Ni(Rb.SO_4)_2$ solution (0.0727M).

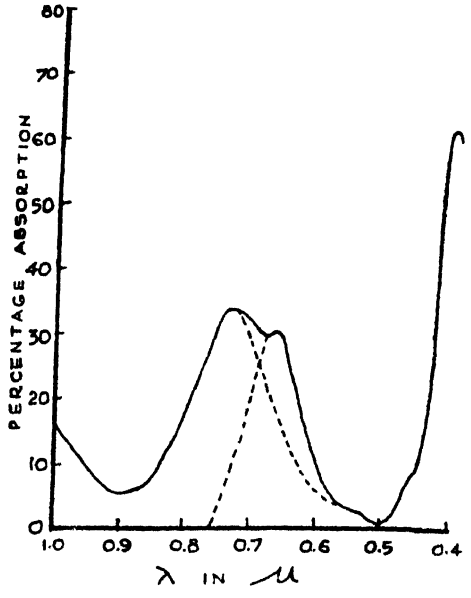

Fig. 8. Absorption curve of $Ni(NH_4SeO_4)_2$ solution (0.0818M).

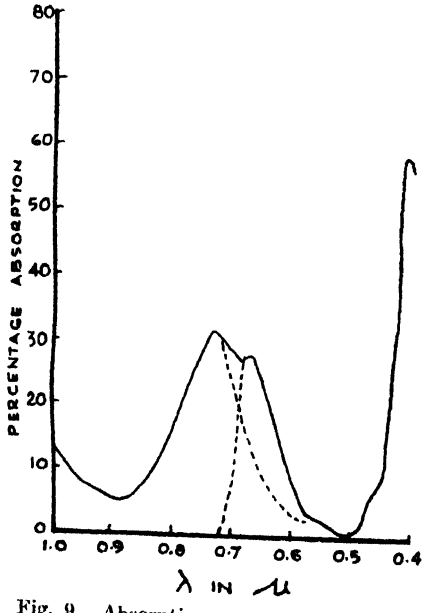

Fig. 9. Absorption curve of $Ni(K.SeO_4)_2$ solution (0.0753M).

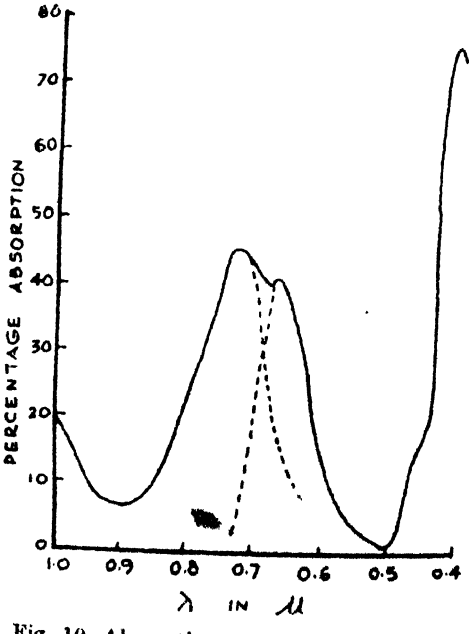

Fig. 10, Absorption curve of $NiCl_2$ solution (0.1252M).

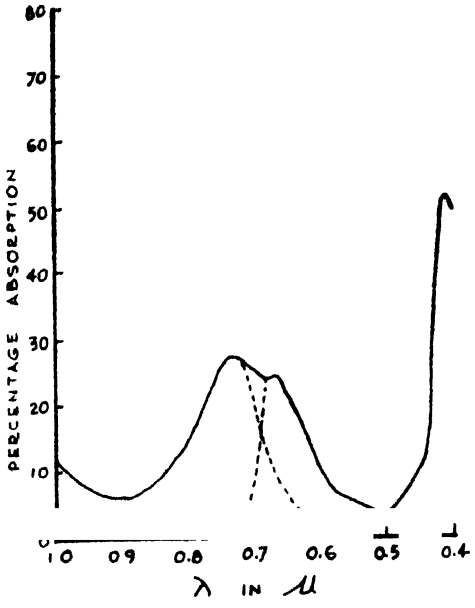

Fig. 11. Absorption curve of $NiBr_2$ solution (0.0613M).

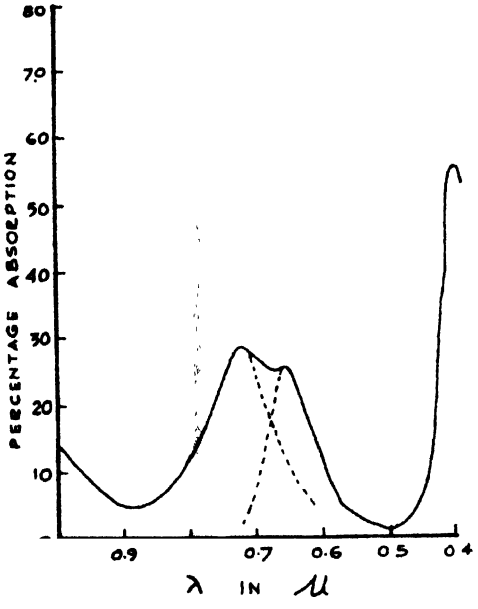

Fig. 12. Absorption curve of $Ni(NO_3)_2$ solution (0.0688M).

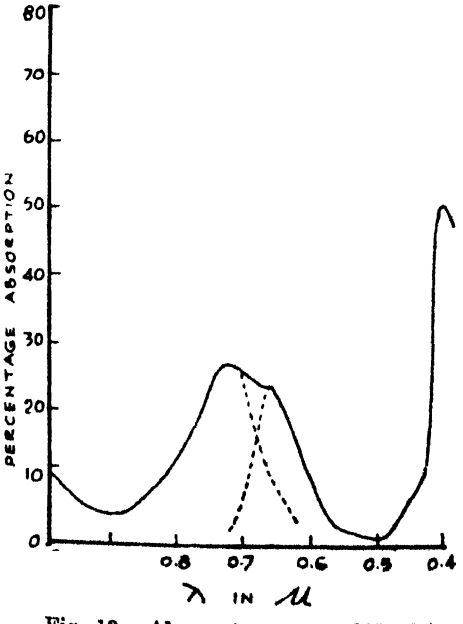

Fig. 13. Absorption curve of $Ni_3Bi_2(NO_3)_{12}$ solution (0.0348M)

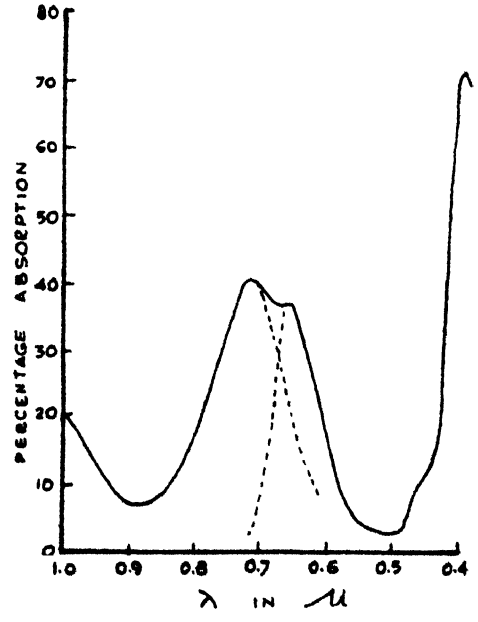

Fig. 14. Absorption curve of $Ni(HCOO)_2$ solution (0.0906M)

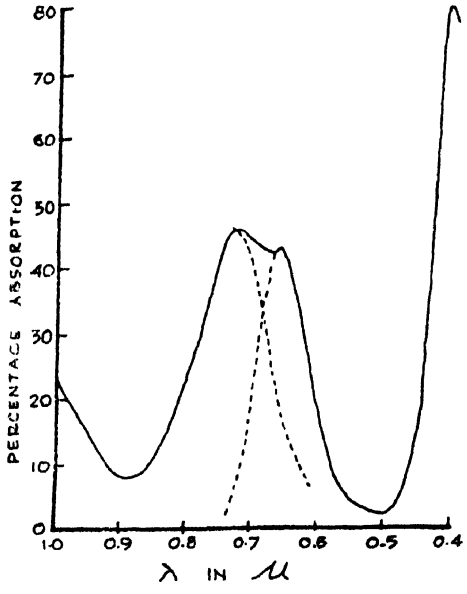

Fig. 15. Absorption curve of $Ni(CH_3C00)_2$ solution (0.154M)

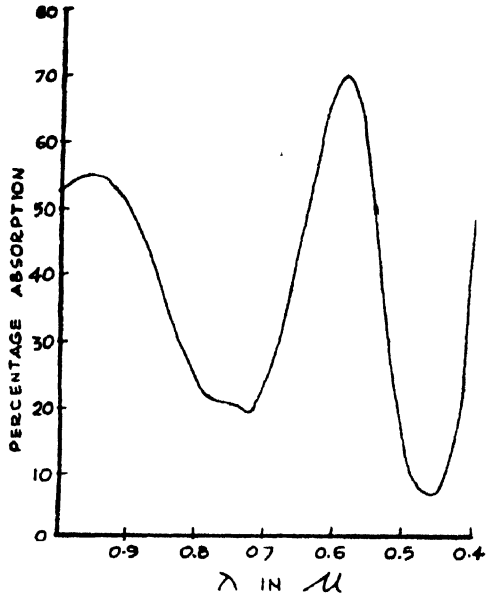

Fig. 16. Absorption curve of $[Ni(NH_3)_4](SO_4)$ (0.08M)

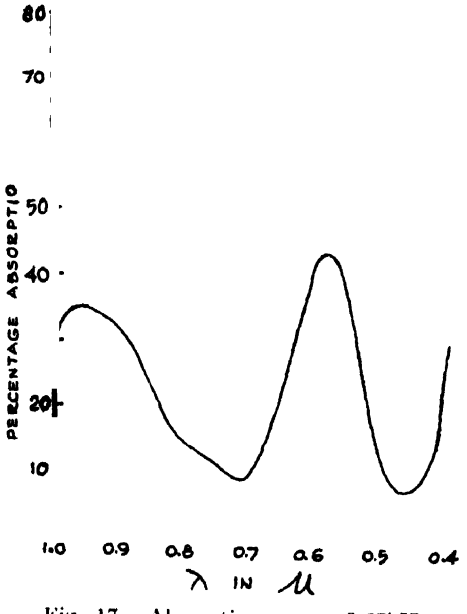

Fig. 17. Absorption curve of $[Ni(NH_3)_4](OH)$ (0.162M)

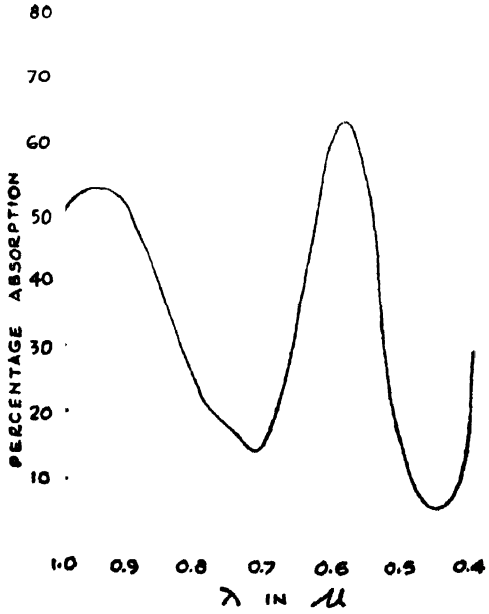

Fig. 18. Absorption curve of $[Ni(NH_3)_4](Cl)$ (0.084M)

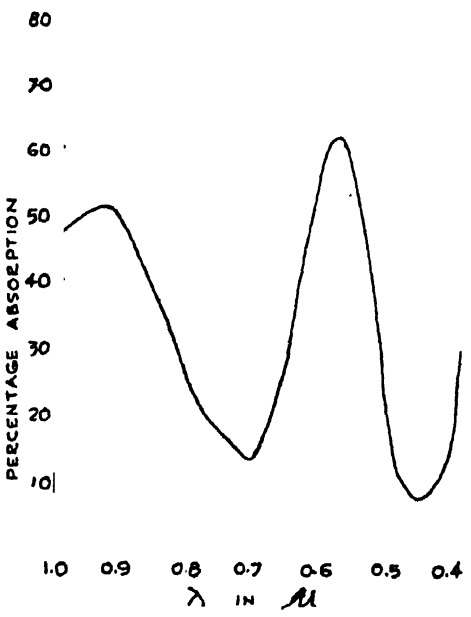

Fig. 19. Absorption curve of $[Ni(NH_3)_4](CH_3C00)_2$ (0.103M)

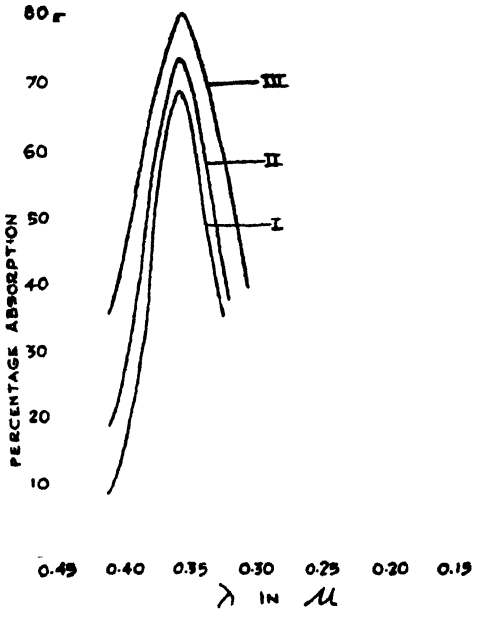

Fig. 20. Absorption curves of
(I) $[Ni(NH_3)_4](SO)_4$ (0.0712M)
(II) $[Ni(NH_3)_4](Cl)$ (0.084M)
(III) $[Ni(NH_3)_4](CH_3C00)_2$ (0.077M)

litre per cm. thickness of the solution. The values of $\delta(-)$ and $\delta(+)$ were obtained by a Gaussian analysis and hence P-values could be calculated. These are given in Table I. K, the cubic field coefficient, are taken from Mookherji and Chhonkar (1960).

DISCUSSION

For all the salts studied the absorption spectra are characterised by three band maxima II, III and IV.

An estimation of the P-values following Van Vleck (1937) and Chhonkar (1964) for the bands II, III and IV are given in Table I.

Most of the theoretical workers subjected Ni^{++} ion to a crystal field of cubic symmetry. Under such a field the ground state $^3F_4$ splits into three levels. Consequently there should be only two absorption band heads. But experimentally three bands were observed. This made these workers to attribute the splitting of the red band due to first order $L-S$ coupling or due to second order intermixing effect.

If this splittings was due to L—S coupling it would have been observed for all the twelve sats of Ni^{++} ion studied by us. But no such splitting could be observed in Nickel amino salts. According to Jörgensen (1958) first order L—S coupling is not capable of accounting for this splitting.

TABLE I

Salt	Band Head	Absorption density	C	$\delta(-)$	$\delta(+)$	$P\times10^5$	K
$NiSO_4$	II	.240	.1068	1250	1720	3.07	17,725
	III	.210		1120	1200	2.10	
	IV	.575		1780	1780	8.82	
$Ni(K.SO_4)_2$	II	.195	.0913	1250	1720	2.91	17,745
	III	.172		720	1200	1.67	
	IV	.523		1780	1780	9.60	
$Ni(NH_4SO_4)_2$	II	.152	.0760	1150	1740	2.66	17,745
	III	.132		740	1160	1.51	
	IV	.366		1540	1540	6.82	
$Ni(RbSO_4)_2$	II	.171	.0727	1350	1420	3.00	17,725
	III	.150		860	1110	1.87	
	IV	.406		1790	1790	9.20	
$NiSeO_4$	II	.285	.1290	1350	1530	2.91	17,725
	III	.244		930	1180	1.84	
	IV	.674		1510	1510	7.26	
$Ni(KSeO_4)_2$	II	.162	.0753	1330	1330	2.65	17,725
	III	.140		600	1200	1.54	
	IV	.377		1516	1570	6.96	
$Ni(NH_4SeO_4)_2$	II	.177	.0818	1330	1330	2.65	17,725
	III	.154		1120	1200	1.99	
	IV	.409		1510	1510	6.95	
$NiCl_2$	II	.263	.1252	1480	830	2.23	17,725
	III	.229		1040	1130	1.83	
	IV	.640		2060	2060	9.69	
$NiBr_2$	II	.137	.0613	1350	830	2.17	17,725
	III	.120		700	1200	1.71	
	IV	.312		1510	1510	7.07	
$Ni(NO_3)_2$	II	.149	.0688	1250	1250	2.49	17,725
	III	.130		620	1440	1.79	
	IV	.347		1510	1510	7.01	
$Ni_3Bi_2(NO_3)_{12}$	II	.134	.0348	1250	1000	3.99	17,745
	III	.114		650	1250	2.87	
	IV	.307		1300	1300	10.55	
$Ni(HCOO)_2$	II	.227	.0906	1190	1530	3.13	17,725
	III	.200		440	1510	1.98	
	IV	.544		1510	1510	8.38	
$Ni(CH_3COO)_2$	II	.269	.1540	1390	1270	2.14	17,725
	III	.241		810	1460	1.62	
	IV	.664		1510	1510	5.99	
$Ni(NH_3)_4SO_4$	II & III	.495	.0800	2120	1950	11.60	22,115
	IV	.509	.0712	1810	2530	14.20	
$Ni(NH_3)_4Cl_2$	II & III	.440	.0840	1760	1480	7.75	22,470
	IV	.582		2140	2990	16.30	
$Ni(NH_3)_4(CH_3COO)$	II & III	.431	.1030	2010	2220	8.17	22,512
	IV	.710	0770	3090	3970	29.90	

If the splitting is attributed to second order intermixing, then greater the cubic field splitting the greater would have been this splitting. But our experimental finding is that in the Nickel amino salts where K, the cubic field coefficient is $\sim$ 22,000 cm^{-1} this splitting is absent, whereas in Tutton salts where $K \sim$ 17,000 cm^{-1} this splitting has been observed and is $\sim$ 1300 cm^{-1}.

Now coming to the question of oscillator strength of these bands we find that the group of salts having K values $\sim$ 22,000 cm^{-1} have greater P-values than those having K-values $\sim$ 17,000 cm^{-1} (Table I). Table I further shows that in Nickel Tutton salts P-values are different from those of nitrate and formate of Nickel and Amino salts. This clearly indicates that though the salts are in state of aqueous solution yet the environments about the absorbing Ni^{++} ion are not the same.

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